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C^{13} and Deuterium Isotope Effects in the Photolysis of Methyl and Ethyl Bromide†

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Relative rates of formation of isotopic radicals in the photolysis of gaseous methyl and ethyl bromide have been measured. Photolyses (2537 A) were carried out in a large excess of cyclopentane. Methyl (or ethyl) radicals formed in the primary C—Br bond scission abstract H from cyclopentane to form methane (or ethane). For methyl bromide, the C^{12}/C^{13} enrichment factor for the first fraction of the methane was 1.039 ± 0.003. The corresponding factor for the α-carbon—Br rupture in ethyl bromide was 1.041 ± 0.004. In the deuterium experiments, CH_3Br—CD_3Br mixtures in excess cyclopentane were photolyzed. The H/D fractionation factor (based on CH_4/CD_3H) was 1.41 ± 0.01.

The difference in rates of formation of isotopic radicals is due to the difference in ultraviolet absorption coefficients of the isotopic alkyl bromides. At 2537 A the observed ratio of the extinction coefficient of CH_3Br relative to that of CD_3Br is 1.38 ± 0.05.

I. INTRODUCTION

Hydrogen halides and alkyl halides dissociate upon absorption of ultraviolet light yielding hydrogen atoms (or alkyl radicals) and halogen atoms. It is known[1] that the quantum yield of hydrogen formation in the photolysis of HBr in the presence of mercury vapor is unity. Friedman *et al.*[2] found that the quantum yield of ethane formation in the photolysis of ethyl bromide (using a full mercury arc) in the presence of mercury vapor and excess cyclopentane was close to 1.0 at room temperature. They also found that the ratio of the rate constants for production of the light and heavy isotopic radicals $C^{12}H_3C^{12}H_2\cdot$ and $C^{12}H_3C^{13}H_2\cdot$ was greater than unity. The isotopic fractionation[3] was attributed to the difference in the extinction coefficients of the isotopic ethyl bromide molecules in the long wavelength region of the spectrum.

Bates *et al.*[4] have shown that the long wavelength extinction coefficient of HBr is appreciably greater than that of DBr (similarly for HI and DI). Gordus and Bernstein[5] found similar results in the case of CH_3Br and CD_3Br. This effect is associated primarily with the difference in zero-point energy of the isotopic molecules in the ground state.

According to reference 2, the isotope fractionation should be appreciably greater for photoillumination consisting of monochromatic 2537-A radiation than for irradiation with a full mercury arc (which emits a considerable fraction of its energy in the shorter wavelength region). In the experiments reported here, mixtures of methyl (or ethyl) bromide in excess cyclopentane were irradiated by means of a mercury resonance lamp (2537 A) and the isotopic composition of the methane (or ethane) produced was measured. Quantitative agreement between the ratio of the extinction coefficients and the CH_3/CD_3 fractionation factor was obtained in the CH_3Br—CD_3Br system.

II. EXPERIMENTAL

Phillips Research Grade cyclopentane was purified by treatment with concentrated sulfuric acid, aqueous bicarbonate, $CaCl_2$, and passage through activated alumina and silica gel. It was then distilled in a 12-in. Vigreaux column and stored in the dark. Baker and Adamson ethyl bromide was purified in a similar manner. Matheson methyl bromide (stated purity 99.4%) was passed through a P_2O_5 column and subjected to trap-to-trap distillation (−78 to −195°C). (It was determined that, relative to a sample of tank CO_2, the ethyl and methyl bromides were depleted in C^{13} by 0.3% and 2.0%, respectively.) The deuterated methyl bromide was a portion of the sample used for the determination of the CD_3Br ultraviolet absorption spectrum,[5] distilled (trap-to-trap) before use.

Cyclopentane and ethyl bromide were measured volumetrically as liquids. Methyl bromide was measured manometrically. A mixture of CH_3Br and CD_3Br was prepared in the (manometric) ratios of 10.0 to 1 and 6.64 to 1. These values were confirmed (±1%)

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[1] E. Warburg, Sitzber. preuss. Akad. Wiss. Physik-math. Kl. **1916,** 314.

[2] Friedman, Bernstein, and Gunning, J. Chem. Phys. **26,** 528 (1957). More complete details are given in the Ph.D. thesis of H. L. Friedman, Illinois Institute of Technology, Chicago (1956).

[3] As early as 1920, T. Merton and H. Hartley [Nature **105,** 104 (1920)] suggested the possibility of a photolytic isotope separation based on a difference in the absorption spectra of isotopic chlorine molecules. W. Kuhn and H. Martin [Naturwissenschaften **20,** 772 (1932); Z. physik. Chem. **B21,** 93 (1933)] observed an enrichment of Cl^{35} in the photolysis of phosgene at 2816 A. A. Farkas and L. Farkas [Trans. Faraday Soc. **34,** 1120 (1938)] reported substantial hydrogen-deuterium separation factors in photochemical reactions liberating hydrogen from aqueous solutions. H. C. Urey [Manhattan District Declassified Document A-750 (July 10, 1943)] discussed aspects of the problem of the photochemical separation of uranium isotopes.

[4] Bates, Halford, and Anderson, J. Chem. Phys. **3,** 415, 531 (1935).

[5] A. A. Gordus and R. B. Bernstein, J. Chem. Phys. **22,** 790 (1954).

TABLE I. C^{12}/C^{13} fractionation results.

Compound and irradiation	Observed fractionation factor, S, for first alkane fraction
C_2H_5Br; 2537 A	1.0163, 1.0235, 1.0200, 1.0206, 1.0202, 1.0251, 1.0194 av $1.020_7 \pm 0.002$
C_2H_5Br; full arc	1.0052, 1.0035, 1.0038 av $1.004_2 \pm 0.001$
CH_3Br; 2537 A	1.0407, 1.0429, 1.0373, 1.0361, 1.0355 av $1.038_5 \pm 0.003$
CH_3Br; full arc	1.0050, 1.0056, 1.0057, 1.0080, 1.0051 av $1.005_9 \pm 0.001$

mass spectrometrically. It is to be noted that the original "CD_3Br" contained 7.35% CD_2HBr and 0.21% CDH_2Br (mass-spectrometric analysis). Cognizance was taken of this fact in calculating the manometric ratios of CH_3Br/CD_3Br.

The alkyl halide and an approximately tenfold excess of cyclopentane were transferred as gases through gold foil (to remove any possible Hg) to the reaction system which consisted of a loop of Pyrex glass tubing with a reaction zone of either Vycor (Corning 7910 glass) for the 2537-A irradiations or quartz for the full arc experiments. The mercury lamp was placed adjacent to the reaction zone. Cycling of the gaseous mixture through the reaction zone was achieved by thermal convection using a tape heater wrapped around one vertical section of the loop. The reaction zone was maintained at room temperature by an air stream. The reaction was normally allowed to proceed to about 5% of completion resulting in *ca* 0.5 cc atmos of alkane product.

When ethyl bromide-cyclopentane mixtures were irradiated, the only alkane product was ethane.[2] Following the irradiation, the contents of the reactor were passed into a trap at −195°C and the very small amount of hydrogen produced in the reaction was pumped off. The trap temperature was then raised to −160°C, liberating ethane which was condensed in another part of the system and measured manometrically. Combustion to CO_2 was achieved by cycling the ethane through CuO, first at 750°C, then at 300°C. After freezing out the water, the CO_2 was measured and transferred to a sample tube for mass-spectrometric assay (C^{12}/C^{13} ratio).

After the irradiation of methyl bromide-cyclopentane mixtures, it was necessary only to pass the contents of the reactor into a trap at −195°C. Only methane (and any very small amount of hydrogen) passed through and was transferred by a Toepler pump to the measuring volume. When normal isotopic methyl bromide was used, the resultant methane was burned to CO_2 (for C^{12}/C^{13} analysis) following procedures similar to those described in the foregoing. In the experiments using CH_3Br—CD_3Br mixtures, the CH_4—CD_3H products were transferred to a break-seal ampoule for direct mass-spectrometric analysis.[6]

Comparison of the ratio of C^{12}/C^{13} in the CO_2 from the combustion of the alkane with that in the CO_2 from the quantitative combustion of the original alkyl bromide yields the fractionation factor, S (see reference 2). A Nier-type isotope-ratio mass spectrometer was used to measure $m/e=44/45$ peak ratios for all samples relative to the reference tank CO_2. The C^{12}/C^{13} fractionation factor is defined in the usual manner:

$$S=\frac{(44/45)\text{ alkane}}{(44/45)\text{ alkyl bromide}}. \tag{1}$$

The methane produced in the photolysis of CH_3Br—CD_3Br mixtures was examined with a Consolidated 21–103 mass spectrometer. Mohler, Dibeler, and Quinn[7] reported that the sensitivities of the molecule ions CH_4^+ and CD_3H^+ are equal within ±2%. This was checked using a sample of CD_3H (obtained from the Volk Radiochemical Company, Chicago, Illinois; 98 atom% D). It was found that the ratio of the parent peak sensitivities CH_4^+/CD_3H^+ was 1.02 ± 0.02 (after correcting for the CD_2H_2 impurity in the CD_3H).

All peaks were corrected for C^{13}; the CH_4^+ and CD_3H^+ peaks ($m/e=16$ and 19) were used in determining the CH_3/CD_3 fractionation factor:

$$S=\frac{[CH_4]/[CD_3H]}{[CH_3Br]/[CD_3Br]}. \tag{2}$$

III. RESULTS

Table I lists values of the observed fractionation factor, S, for the first alkane fraction for the ethyl and methyl bromide C^{12}/C^{13} fractionation experiments. The results corrected[2] to zero extent of reaction, S^0, would be equal to S within the limits of accuracy of the experimental results because of the low extent of reaction.

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[6] In preliminary experiments (results not reported herein) the isotopic methanes were transferred to a sample tube, the stopcock of which was coated with silicone high-vacuum grease. Some of these samples showed abnormally high and erratic ratios of CH_4/CD_3H, perhaps as a result of conversion to CD_2H_2 through some post-irradiation exchange reaction. Attempts to determine quantitatively whether any excess CD_2H_2 was present were not wholly successful due to the variable residual water background at $m/e=18$ in the mass spectrometer. The origin of spuriously high ratios of CH_4 to CD_3H could have been via a radical exchange reaction [Lavrovskaia, Mardaleishvili, and Voevodskii, Voprosy Khim. Kinetiki, Kataliza, i Reaktsionnoĭ Sposobnosti Akad. Nauk SSSR., Otdel, Khim. Nauk, 40–53 (1955). (Technical Translation TT-701, Natl. Research Council of Canada) Nuclear Sci. Abstr. **12,** 4097(A) (1958)] $CD_3\cdot + H_2 = CD_2H\cdot + HD$ possibly occurring during the irradiation. Such a reaction, however, must have been of negligible importance in the present case, since the amount of molecular hydrogen in the products was generally less than 0.01% of the total amount of the reactants.

[7] Mohler, Dibeler, and Quinn, J. Research Natl. Bur. Standards, **61,** 171 (1958).

The results of the photolyses of the CH_3Br—CD_3Br mixtures, corrected[2] to zero extent of reaction, S^0, are listed in Table II.

IV. DISCUSSION

In this region of the spectrum the absorption of light by an alkyl halide molecule results in dissociation into an alkyl radical and a bromine atom. The abstraction of hydrogen from cyclopentane by the alkyl radical to form an alkane is a fast reaction. It is seen that, for zero extent of reaction (considering as an example the CH_3Br—CD_3Br system),

$$\frac{\{(d/dt)[CH_3\cdot]\}_0}{\{(d/dt)[CD_3\cdot]\}_0}=\frac{[CH_3\cdot]_0}{[CD_3\cdot]_0}=\frac{[CH_4]_0}{[CD_3H]_0}$$

$$=\frac{\Phi_H I_{H\ \mathrm{abs.}}}{\Phi_D I_{D\ \mathrm{abs.}}}=\frac{\Phi_H\epsilon_H[CH_3Br]_0}{\Phi_D\epsilon_D[CD_3Br]_0}. \qquad (3)$$

Therefore,

$$S^0=\frac{\Phi_H\epsilon_H}{\Phi_D\epsilon_D}, \qquad (4)$$

using the definition of S from Eq. (2). Here Φ_H represents the quantum yield, I_H the absorbed light intensity, and ϵ_H the extinction coefficient for the CH_3Br (the subscript D refers to CD_3Br).

Equation (4) will be valid if the following conditions are met. First, the extent of reaction must be kept low and uniform throughout the reaction zone; rapid circulation and thorough mixing is implied. Second, radical exchange reactions such as $(CH_3)^*\cdot+CH_3Br=(CH_3)^*Br+CH_3\cdot$ must not occur to any appreciable extent.

The latter condition is assured by the use of a considerable excess of cyclopentane; variation in the ratio of cyclopentane to alkyl bromide from 1:1 to 30:1 had no systematic influence on the magnitude of the fractionation factors. The thoroughness of mixing is more difficult to evaluate; possibly the low values of the enrichment factors in certain of the C^{13} experiments were associated with inadequate mixing.

Since the quantum yields for dissociation of the alkyl halides are close to, if not equal to unity,[2] and probably identical in any case for two isotopic alkyl halides, the fractionation factor is then equal to the ratio of the extinction coefficients of the parent isotopic molecules.

TABLE II. CH_3Br/CD_3Br fractionation results.

CH_3Br/CD_3Br mixture	Fractionation factor, S^0
10.0:1	1.40_0
6.64:1	1.41_7
6.64:1	1.42_8
6.64:1	1.41_8
6.64:1	1.40_0
	av $1.41_3\pm0.01$

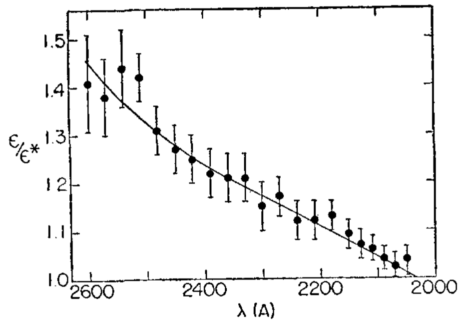

FIG. 1. Ratio of extinction coefficients (ϵ/ϵ^*) *vs* wavelength λ(A) for CH_3Br relative to "CD_3Br" sample (containing 7.35% CD_2HBr, 0.21% CDH_2Br) of reference 5. Experimental points from reference 5, Table 2. Solid line calculated (see text).

For ethyl bromide photolyses with the full arc, Friedman *et al.*[2] obtained a value of $S=1.007\pm0.001$ (based on CO_2 from the combustion of ethane). The difference between that and the present value of 1.004 ± 0.001 is probably due to a different intensity-wavelength distribution from the different mercury arc lamps used. A small increase in the short wavelength contribution from the lamp would account for the reduced C^{12}/C^{13} fractionation.

For the 2537-A photolyses of ethyl bromide the average value of S was 1.020_7 (Table I). To a good approximation only the α-carbon atom (bonded to the Br) is involved in the C^{12}/C^{13} isotope effect; the β-carbon remains unaffected and merely serves to "dilute" the C^{12} enrichment in the CO_2 obtained from combustion of the ethane by a factor of two.[8] Thus, the ratio of the rate constants for the production of $C^{12}H_3C^{12}H_2\cdot$ to $C^{12}H_3C^{13}H_2\cdot$ is 1.041_4 for 2537-A irradiation *versus* 1.008 for the full arc. In the case of methyl bromide, the fractionation factor of 1.038_5 is a direct measure of the relative rate constants for production of $C^{12}H_3\cdot$ and $C^{13}H_3\cdot$ by photolysis at 2537 A. For the full arc, the C^{12} fractionation factor (1.006) is also comparable to the above value (1.008) for ethyl bromide.

The deuterium isotope effect in the CH_3Br—CD_3Br mixtures may be directly compared with the ratio of the extinction coefficients of the two compounds. Figure 1 shows the ratio of the extinction coefficient of CH_3Br to that of the original "CD_3Br" sample as a function of the wavelength. The experimental points are those of reference 5, Table 2. The solid line from 2040 to 2360 A was calculated from Eq. (1), reference 5; from 2360 to 2600 A, it is based upon a re-examination of the original data,[5] combined with recent confirmatory measurements on CH_3Br in this region. At 2537 A, ϵ/ϵ^* is 1.36_5 with an estimated uncertainty of ±0.05. Correcting this ratio for the CD_2HBr and

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[8] This assumes random distribution of carbon isotopes in the ethyl bromide. It can be shown that small (*ca* 2%) differences in the C^{13} content of the two carbon positions will not noticeably affect the correction factor of 2.0.

CDH_2Br content of the sample, a ratio of $\epsilon(CH_3Br)/\epsilon(CD_3Br)$ of 1.38 ± 0.05 is calculated.[9] The agreement of this value with that obtained in the deuterium fractionation experiments leads to the conclusion that the difference in rates of formation of isotopic radicals is due to the difference in ultraviolet absorption coefficients of the isotopic alkyl bromides. With the use of the photolytic isotope fractionation technique, it thus appears possible to deduce the absorption spectrum of the less abundant isotopic species from that of the natural isotopic mixture.

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[9] The correction was made as follows: Let

$$\epsilon(CDH_2Br)/\epsilon(CH_3Br)=\alpha_1;$$

$$\epsilon(CD_2HBr)/\epsilon(CH_3Br)=\alpha_2;$$

$$\epsilon(CD_3Br)/\epsilon(CH_3Br)=\alpha_3.$$

It was assumed that $\alpha_3=\alpha_1^3$ and $\alpha_2=\alpha_1^2$. Thus, using the previously quoted values of the mole fractions of each deuterated species: $1/1.365=(0.9244)\alpha_3+(0.0735)\alpha_2+(0.0021)\alpha_1$. Thus, $\alpha_3=1/1.38$.

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Zeeman Effect in the 1- to 3-Millimeter Wave Region: Molecular *g* Factors of Several Light Molecules

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The Zeeman effect has been observed in the microwave rotational spectra of several light molecules, and the high-frequency limit of such measurements has been extended for the first time to 1.1 mm wavelength. The magnitudes of the molecular g factors g_J and, where applicable, the components of the g tensor lying along the principal axes of rotation, have been obtained for DBr, DI, CO, PH_3, PD_3, SO_2, O_3, H_2S, HDS, and D_2S. When combined with information from other sources the data have permitted, in addition, a determination of the sign of g_J for DBr and DI, and of the sign of the electric dipole moment of DI.

MICROWAVE spectral observations in the region from 1- to 3-mm wavelength have been made with increasing frequency during the last few years. The necessary power in the region has been obtained most often from crossed wave guide silicon crystal harmonic producers driven by klystrons operating in the vicinity of 1 cm wavelength. Improvements made by R. S. Ohl of this laboratory in the treatment of silicon crystals for this application have now made feasible certain types of measurements which, while heretofore possible, were usually impractical in the shorter wavelength area of this region. Two of these are the observation of the Stark and the Zeeman effects in the rotational spectra of light molecules. These observations, because of the extra loss in the special absorption cells required, and because the effects result in the splitting of the absorption lines into, often, several components, require more mm wave power than is necessary for determination of the absolute frequency of the unsplit lines.

We have reported studies, extending to 1.1 mm wavelength, of the Stark effect in certain light molecules[1,2]; we now wish to describe the results of a study which demonstrates the feasibility of measurement, into the 1-mm wave region, of the Zeeman effect. In this work a conventional Zeeman spectrometer has been used for the observation of low-J transitions in DBr^{79}, DBr^{81}, DI^{127}, CO, PH_3, PD_3, SO_2, O_3, H_2S, HDS, and D_2S, at frequencies to 267 000 Mc. Except in the case of the two isotopes of phosphine, in which no splitting was observable at the maximum available fields, and thus where only an upper limit could be assigned to the g factor, splittings in all cases were sufficient to resolve both π and σ components, and the magnitudes of the molecular g factors have been evaluated. In the case of DBr and DI, where the sign of the nuclear g factor of the halogens involved is known from other sources, the sign of the molecular g factor has also been found. In addition, our data on DI, coupled with information on TI from other sources, have led to a determination of the sign of the electric dipole moment of hydrogen iodide.

EXPERIMENTAL PROCEDURE

The method of producing and detecting power in the shorter mm wave region, and the method of frequency

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[1] C. A. Burrus and J. D. Graybeal, Phys. Rev. **109**, 1553 (1958).

[2] C. A. Burrus, J. Chem. Phys. **28**, 427 (1958).